

Chemical Studies on the Uses of Urea Complexes to Synthesize Compounds Having Electrical and Biological Applications

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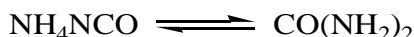
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Abstract- The chelation of urea (U) with silver(I), chromium(III), cadmium(II) and zinc(II) ions at different state of temperatures has been studied by elemental analyses, magnetic susceptibility, conductivity measurements, (infrared and ¹H-NMR) spectra, thermal analysis (TG/DTG), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), and x-ray powder diffraction (XRD). The high values of molar conductivity of the resulting urea complexes show them to be electrolytes in nature. The physical and spectral data were well explained in terms of the formation of AgNO₃.2U.6CH₃OH (1), AgNO₃.2U.CH₃OH (2) and Ag metal (3) for silver(I), CrCl₃.2U.12H₂O (4), CrCl₃.4U.9H₂O (5) and Cr₂O₃ (6) for chromium(III), CdCl₂.2U. H₂O (7), CdCl₂.4U.H₂O (8) and CdO (9) for cadmium(II) and ZnCl₂.4U.4H₂O (10), ZnCl₂.2U.6H₂O (11) and ZnO (12) for zinc(II). Complexes of urea (1, 4, 7 and 10), (2, 5, 8 and 11) and (3, 6, 9 and 12) were synthesized at room, 60°C and 800°C, respectively. On the basis of the infrared spectral data and the values of stretching vibrational bands of both –C=O and –NH₂ groups, the complexation of metal ions toward urea was distinguished. The enhancement of the microbial treatments against bacteria (*Escherichia Coli*, *Staphylococcus Aureus*, *Bacillus subtilis* and *Pseudomonas aeruginosa*) and fungi (*Aspergillus Flavus* and *Candida Albicans*) was assessed and recorded remarkable efficiency.

Keywords- Urea; Transition Metals; Biological Activity; Conductance; Spectroscopic Studies; Thermal Analysis

I. INTRODUCTION

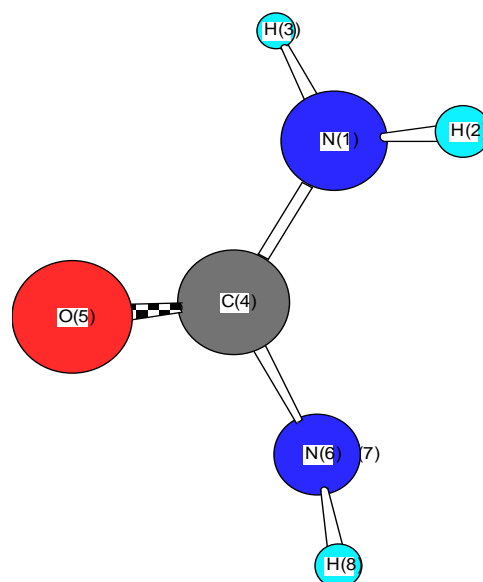
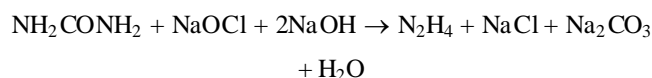
Carbamide, carbonyldiamide or the most famous name, urea (Scheme 1), CH₄N₂O, was first prepared by Wöhler^[1] by evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate. Ammonium isocyanate, which is formed first, undergoes molecular rearrangement to give urea, as shown by the following reaction:



Urea may be prepared in the laboratory by the interaction of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. Industrially^[2-4], urea is prepared by allowing liquid carbon dioxide and liquid ammonia to interact, and heating the formed ammonium carbamate at 130 ~ 150 °C under about 35 atmospheric pressure. The carbamate is decomposed to form urea and water according to the following reaction;



Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Adults excrete about 30 g of urea per day in the urine, from which it can be extracted by evaporating the urine to small volume and adding nitric acid, to give the slightly soluble urea nitrate, CO(NH₂)₂.HNO₃. Urea has a melting point of 132°C, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-Urea resin (plastics)^[5], barbiturates^[6], and fertilizers^[7-10]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine^[11-13]. Recently, urea is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite^[6] e.g.,



Scheme 1 Structure of urea

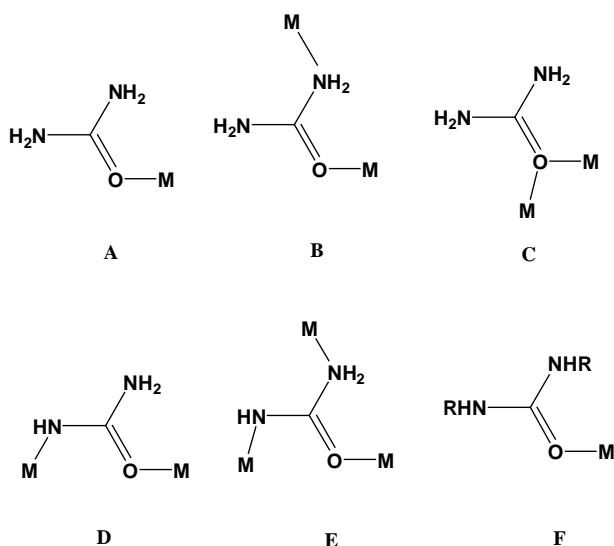
Urea is used in reactive dyeing^[14] which has an effect on the formation and cleavage of covalent bond between the reactive dye and cellulose. The overall effect of urea on reactive dyeing depends on the solvolytic stability of the dye-fiber bond under specific dyeing conditions.

Complexes of urea with some metal ions are used as fertilizers^[15-18]. Complexes of urea with zinc sulphate and

nitrate, $[\text{Zn}(\text{CON}_2\text{H}_4)_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Zn}(\text{CON}_2\text{H}_4)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ have very important application in this field ^[19]. These complexes were found to increase the yield of rice more than a dry mixture of urea-zinc salt does. Calcium nitrate-urea complex, $[\text{Ca}(\text{urea})_4](\text{NO}_3)_2$, ^[20, 21] was used also as an adduct fertilizer. Some metal-urea complexes have pharmaceutical application, e.g., the platinum-urea complex which is used as antitumor ^[22].

Crystal structure studies have shown that in solid urea, both nitrogen atoms are identical. Bond length measurements ^[6] in urea give the C-N distance as 1.37 \AA , while, in aliphatic amines the C-N bond length is 1.47 \AA . This indicates that the C-N bond in urea has some double bond character (about 28%).

Urea usually coordinates as a monodentate ligand through the oxygen atom, forming a $\text{C}=\text{O} \cdots \text{M}$ angle considerably smaller than 180° , in accordance with the sp^2 hybridization of the O atom (**A** in Scheme 2). The rare N, O-bidentate coordination mode (**B** in Scheme 2) has been found in a very limited number of cases ^[23, 24], while in $[\text{Hg}_2\text{Cl}_4\text{U}_2]$ each U molecule bridges the two Hg^{II} atoms through the oxygen atom ^[25] (**C** in Scheme 2). Of particular chemical/biological interest is the ability of U to undergo metal-promoted deprotonation ^[26], the monoanionic ligand H_2NCONH^- adopts the μ_2 (**D** in Scheme 2) and μ_3 (**E** in Scheme 2) coordination modes. The urea and its derivatives such as the N,N'-dimethylurea and N,N'-diethylurea (Scheme 2) have only been found to coordinate as monodentate ligands through the oxygen atom (**F** in Scheme 2).



Scheme 2 The coordination modes of urea towards metal ions

Raman and infrared spectra of urea have been observed by several investigators ^[27-32]. The normal vibrations of the urea molecule were calculated by Kellner ^[33] on the assumption of the non-planar model. However, on the basis of the dichronic measurement of the infrared band arising from the N-H stretching vibration by Waldron and Badger ^[34] and the proton magnetic resonance absorption measurement made by Andrew and Hyndman ^[35], it is

concluded that urea molecule has a planar structure. Yamaguchi et al. ^[36] calculated the normal vibrations of the C_{2v} model of urea molecule as an eight-body problem using a potential function of the Urey-Bradley force field and obtained the force constants which have been refined by the least-squares method. Based on the result of these calculations, Yamaguchi ^[36], assigned all of the observed frequencies in the spectra of urea and urea- d_4 . To the two vibrations of the frequencies 1686 cm^{-1} and 1603 cm^{-1} , there are considerable contributions of both CO stretching and NH_2 bending motions, whereas Stewart ^[37] assigned the 1686 cm^{-1} band to CO stretching vibration and the 1603 cm^{-1} band to NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-1} , the contribution of the NH_2 bending motion is greater than that of CO stretching motion. The band at 1629 cm^{-1} corresponds to almost pure NH_2 bending vibration. The NH_2 bending motion of A_1 type is equal to that of B_2 type. The A_1 type band should have a frequency of about 1630 cm^{-1} , if there is no coupling between NH_2 bending and CO stretching motions. On the other hand, the observed frequency of 1610 cm^{-1} of urea- d_4 is assigned to almost pure skeletal vibration. Therefore, the interaction between the 1630 cm^{-1} and 1610 cm^{-1} vibration gives rise to the two observed bands at 1686 cm^{-1} and 1603 cm^{-1} . The infrared bands of urea- d_4 observed at 1245 cm^{-1} and 1154 cm^{-1} are assigned, respectively, to A_1 type and B_2 type, ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The large frequency difference between the A_1 and B_2 vibrations is due to the fact that in the A_1 vibration, the cross term related to the CN stretching vibration is large.

The 1464 cm^{-1} frequency of urea is assigned to the CN stretching vibration of B_2 type. The corresponding frequency of urea- d_4 is observed at 1490 cm^{-1} . The 1150 cm^{-1} band is assigned to NH_2 rocking vibrations of both A_1 and B_2 types. The normal vibration calculation yields almost the same values for these frequencies.

Urea possesses two types of potential donor atoms, the carbonyl oxygen and amide nitrogens. Penland et al. ^[38] studied the infrared spectra of urea complexes to determine whether coordination occurred through oxygen or nitrogen atoms. The electronic structure of urea may be represented by a resonance hybrid of structures **A-F** as shown in scheme 1 with each contributing roughly an equal amount. If coordination occurs through nitrogen, contributions of structure **B** will decrease. This results in an increase of the CO stretching frequency with a decrease of CN stretching frequency. The N-H stretching frequency in this case may fall in the same range as those of the amido complexes. If coordination occurs through oxygen, the contribution of structure (**A**) will decrease. This may result in a decrease of the CO stretching frequency but no appreciable change in NH stretching frequency. Since the vibrational spectrum of urea itself has been analyzed completely ^[36], band shifts caused by coordination can be checked immediately. For example, the effect of the coordination on the spectra of the complexes of urea with $\text{Pt}(\text{II})$ and $\text{Cr}(\text{III})$ in which the coordination occurs through nitrogen and oxygen atoms, respectively ^[38]. The mode of coordination of urea with

metal ions seems to be dependent upon the type and nature of metal. Pd(II) coordinates to the nitrogen, whereas Fe(III), Zn(II), and Cu(II) coordinate to the oxygen of urea^[38].

In urea-metal complexes, if a nitrogen-to-metal bond is present, the vibrational spectrum of this complex differs significantly from that of the free urea molecule. The N-H stretching frequencies would be shifted to lower values, and the C=O bond stretching vibration ($\nu(\text{C}=\text{O})$) would be shifted to higher frequency at about 1700 cm^{-1} ^[39].

Recently, urea represents not only an important molecule in biology^[40] but also an important raw material in chemical industry^[41]. The aim of this publication is to report the synthesis, characterization, conductance and biological studies of the resulting compounds formed from the reactions of urea with AgNO_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and ZnCl_2 at room, elevated and ignition temperatures.

II. EXPERIMENTAL

A. Materials

Urea, AgNO_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, H_2O , ZnCl_2 and methanol solvent were obtained from Aldrich Company. Urea was received from Fluka chemical company. All chemicals used in this study were of analytically reagent grade and used without further purification.

B. Synthesis of Ag(I), Cr(III), Cd(II) and Zn(II) Urea Complexes

1) Synthesis of Urea Complexes at Room Temperature:

The complexes, $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7) and $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) were prepared by mixing equal methanolic solutions of AgNO_3 (1.70 g, 0.01 mole), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2.67 g, 0.01 mole), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (2.02 g, 0.01 mole) or ZnCl_2 (1.37 g, 0.01 mole) in 25 mL methanol with a 50 mL volume of urea solution (6.0 g, 0.1 mole) in methanol solvent. The mixtures were allowed to be stirred for about 12 hours under refluxed system at room temperature *Ca.* 25°C . In all cases of Ag(I), Cr(III), Cd(II) and Zn(II)-urea mixtures, the products took longer time of precipitation. In all the cases, the amount of the formed precipitate was increased with increasing the time of standing. The colored precipitation complexes formed in each case was filtered off, dried under *vacuo* over anhydrous calcium chloride.

2) Synthesis of Urea Complexes at 60°C :

The urea complexes, $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11), were prepared by a method similar to that described for the preparation of urea complexes at room temperature. A 25 mL volume of urea solution (6.0 g, 0.1 mole) was mixed with an equal volume of Ag(I), Cr(III), Cd(II) or Zn(II) salts solution, AgNO_3 (1.70 g, 0.01 mole), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2.67 g, 0.01 mole), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (2.02 g, 0.01 mole) or ZnCl_2 (1.37 g, 0.01 mole) in 25 mL methanol. The mixtures were stirred for about 2 hours then heated to 60°C for 6 hours on a water bath under refluxed system. The

precipitated products were filtered off, dried at 60°C in an oven for 3 hours and then dried under *vacuo* over anhydrous calcium chloride.

C. Measurements

The elemental analyses of carbon, hydrogen and nitrogen contents were performed by the microanalysis unit at Cairo University, Egypt, using a Perkin Elmer CHN 2400 (USA). The molar conductivities of freshly prepared $1.0 \times 10^{-3}\text{ mol/cm}^3$ dimethylsulfoxide (DMSO) solutions were measured for the soluble urea complexes using Jenway 4010 conductivity meter. Magnetic measurements were performed on the Magnetic Susceptibility Balance, Sherwood Scientific, and Cambridge Science Park-Cambridge-England. The infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$). The $^1\text{H-NMR}$ (400 MHz) spectra were recorded on Varian Gemini Spectrophotometers. The thermal studies TG/DTG-50H were carried out on a Shimadzu thermogravimetric analyzer under static air till 800°C . Scanning electron microscopy (SEM) images and Energy Dispersive X-ray Detection (EDX) were taken in Joel JSM-6390 equipment, with an accelerating voltage of 20 KV. The X-ray diffraction patterns for the urea complexes were recorded on X Pert PRO PANalytical X-ray powder diffraction, target copper with secondary monochromate.

D. Antibacterial and Antifungal Activities

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method^[42]. Briefly, 100 μL of the best bacteria/fungi were grown in 10 mL of fresh media until they reached a count of approximately 108 cells/mL for bacteria and 105 cells/mL for fungi^[43]. 100 μL of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method^[44, 45].

Of the many media available, National Committee for Clinical Laboratory Standards (NCCLS) recommends Mueller-Hinton agar due to: it results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi is tested by using approved standard method (M38-A) developed by the NCCLS^[46] for evaluating the susceptibility of filamentous fungi to antifungal agents. Disc diffusion method for yeast developed standard method (M44-P) by the NCCLS^[47]. Plates inoculated with filamentous fungi as *Aspergillus Flavus* at 25°C for 48 hours; Gram (+) bacteria as *Staphylococcus Aureus*, *Bacillus subtilis*; Gram (-) bacteria as *Escherichia Coli*, *Pseudomonas aeruginosa* they were incubated at $35\text{--}37^\circ\text{C}$ for 24-48 hours and yeast as *Candida Albicans* incubated at 30°C for 24-48 hours and, then the diameters of the inhabitation zones were measured in millimeters^[42]. Standard discs of Tetracycline (Antibacterial agent), Amphotericin B (Antifungal agent) served as positive controls for antimicrobial activity but filter disc impregnated

with 10 μ l of solvent (distilled water, chloroform, DMSO) were used as a negative control.

The agar used is Mueller-Hinton agar that is rigorously tested for composition and pH. Furthering the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition which have been determined for susceptible values. Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated 10 μ l of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar, the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar, it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as a "Zone of inhibition" or "Clear zone". For the disc diffusion, the zone diameters were measured with slipping calipers of the National for Clinical Laboratory Standards [44]. Agar-based methods such as Etest disk diffusion can be good alternatives because they are simpler and faster than broth methods [48, 49].

III. RESULTS AND DISCUSSION

The color, physical characteristic, micro-analytical data, molar conductance measurements of Ag(I), Cr(III), Cd(II) and Zn(II) urea complexes are given in Table 1. The elemental analysis data of some prepared complexes revealed 1 : 2 molar ratio (M:U) (where M = Ag(I), Cr(III), Cd(II) or Zn(II) and U = urea) and good agreement with the general formulas $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11). On the other hand, $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) and $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) complexes formed with 1 : 4 (M : U) molar ratio. It is important to mention that complexes 1, 4, 7, and 10 of urea were prepared at room temperature but urea complexes of 2, 5, 8, and 11 were resulted from the complexation between urea and Ag(I), Cr(III), Cd(II) or Zn(II) ions at 60 °C with molar ratio 4 : 1 (U : M). The reactions can be represented by the stoichiometric equations:

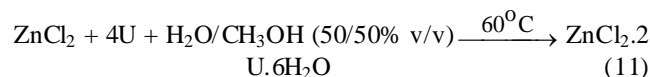
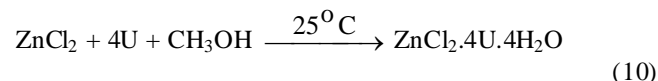
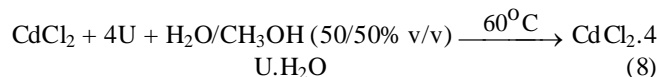
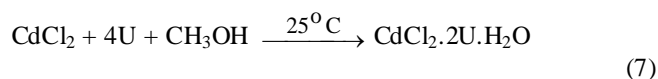
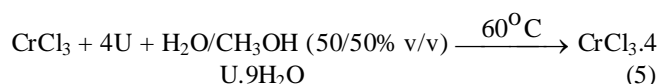
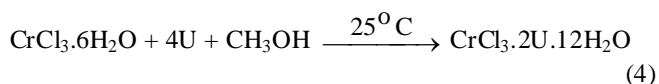
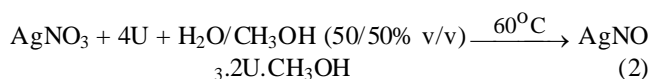
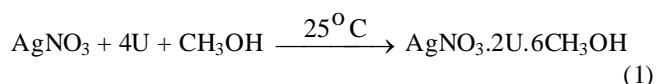


TABLE 1 PHYSICAL CHARACTERIZATION, MICRO-ANALYTICAL AND MOLAR CONDUCTANCE DATA OF UREA COMPLEXES

Complexes Molecular Formula Empirical Formula (MW.)	Color	Molar Ratio	Elemental Analysis (%) Found (Calcd.)		Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
			C	H	
$\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1) 481.87 g/mol	Grey	1:2	19.7 9 (19.92)	6.46 (6.64)	75
$\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2) 321.87 g/mol	Dark grey	1:2	10.7 0 (11.18)	3.70 (3.37)	83
$\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4) 494.55 g/mol	Dark green	1:2	4.70 (4.85)	6.40 (6.47)	154
$\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5) 560.55 g/mol	Green	1:4	8.60 (8.56)	5.94 (6.06)	149
$\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7) 321.32 g/mol	White	1:2	7.60 (7.47)	2.96 (3.11)	98
$\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) 441.32 g/mol	White	1:4	10.7 0 (10.87)	3.98 (4.08)	103
$\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) 448.29 g/mol	White	1:4	10.9 1 (10.71)	5.46 (5.35)	121
$\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) 364.29 g/mol	White	1:2	6.50 (6.59)	6.50 (6.59)	107

The complexes are hygroscopic, low melting points, soluble in H_2O and dimethylsulfoxide, DMSO. The molar conductivities of $10^{-3} \text{ mol dm}^{-3}$ solutions of the prepared complexes in DMSO (Table 1) indicate that the complexes have an electrolytic nature.

A. Molar Conductance Measurements

The molar conductivity values for the urea complexes in DMSO solvent ($10^{-3} \text{ mol dm}^{-3}$) are exhibited in the range of (75–154) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, suggesting them to be electrolytes (Table 1). Conductivity measurements within the limits of their solubility provide a method of testing the degree of ionization of the complexes, the molar ions that a complex liberates in solution (in case of presence anions outside the coordination sphere), the higher will be its molar conductivity and vice versa. It is clear from the conductivity data that the complexes present seems to be electrolytes.

Also the molar conductance values indicate that the anions present outside the coordination sphere. This result was confirmed from the elemental analysis data where Cl^- or NO_3^- ions are precipitated with colored solution by adding of AgNO_3 or FeSO_4 solutions, respectively, this experimental test is well matched with CHN data. All these complexes have electrolytic properties. This fact elucidated that the Cl^- or NO_3^- were present. These results establish the stoichiometry of these complexes, which are in agreement with the general formulas suggested.

B. Magnetic Measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance according to the Gouy method. The calculations were evaluated by applying the following equations:

$$\chi_g = \frac{cl(R - R_o)}{10^9 M}$$

$$\chi_m = \chi_g M W t.$$

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_m T}$$

where χ is mass susceptibility per gm sample

c is the calibration constant of the instrument and equal to 0.0816

R is the balance reading for the sample and tube

R_o is the balance reading for the empty tube

M is the weight of the sample in gm

T is the absolute temperature

The magnetic moments of the $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4) and $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5) complexes at $T = 300$ K and their corresponding hybrid orbitals were calculated. The observed values of the effective magnetic moments μ_{eff} measured for these complexes equal to 2.85 B.M., this is in convenient with experimental values of 3.27 B.M. [50] obtained for octahedral Cr(III) complex with d^2sp^3 hyperdization for both Cr(III)/U complexes.

C. Infrared Spectra

The infrared spectra of the Ag(I), Cr(III), Cd(II) and Zn(II) urea complexes at room, 60°C and 800°C temperature are shown in Figs. 1, 2 and 3, respectively. The band locations were measured for the mentioned urea complexes, together with the proposed assignments for the most characteristic vibrations are presented in Tables 2, 3, 4 and 5. In order to facilitate the spectroscopic analysis and to put our hand on proper structure of the prepared complexes, the spectra of the urea complexes were accurately compared with those of the urea and similar complexes in literature survey. The infrared spectra in the wide frequency range (4000–400 cm^{-1}) are shown in Fig. 1, whereas the region between 1500–to–400 cm^{-1} is focused to urea complexes at 800°C temperatures (Fig. 3). The discussion of the spectra will be addressed on the basis of the most characteristic vibrations.

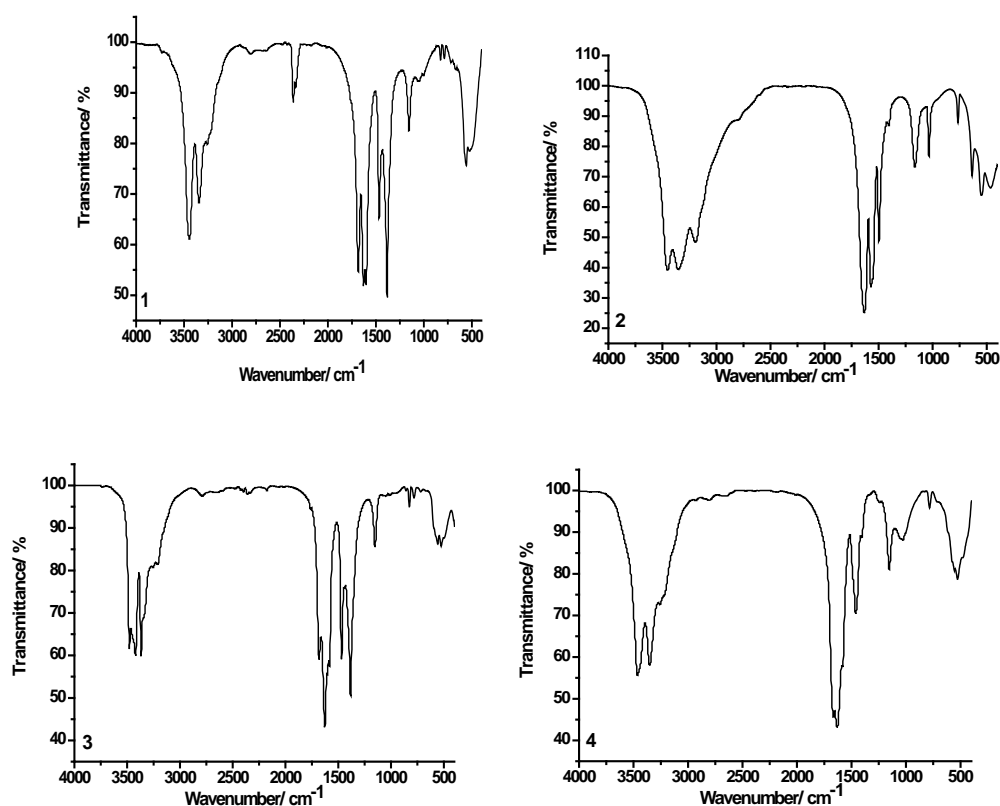


Fig. 1 Infrared spectra of urea complexes at room temperature: $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (2), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (3) and $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ complexes

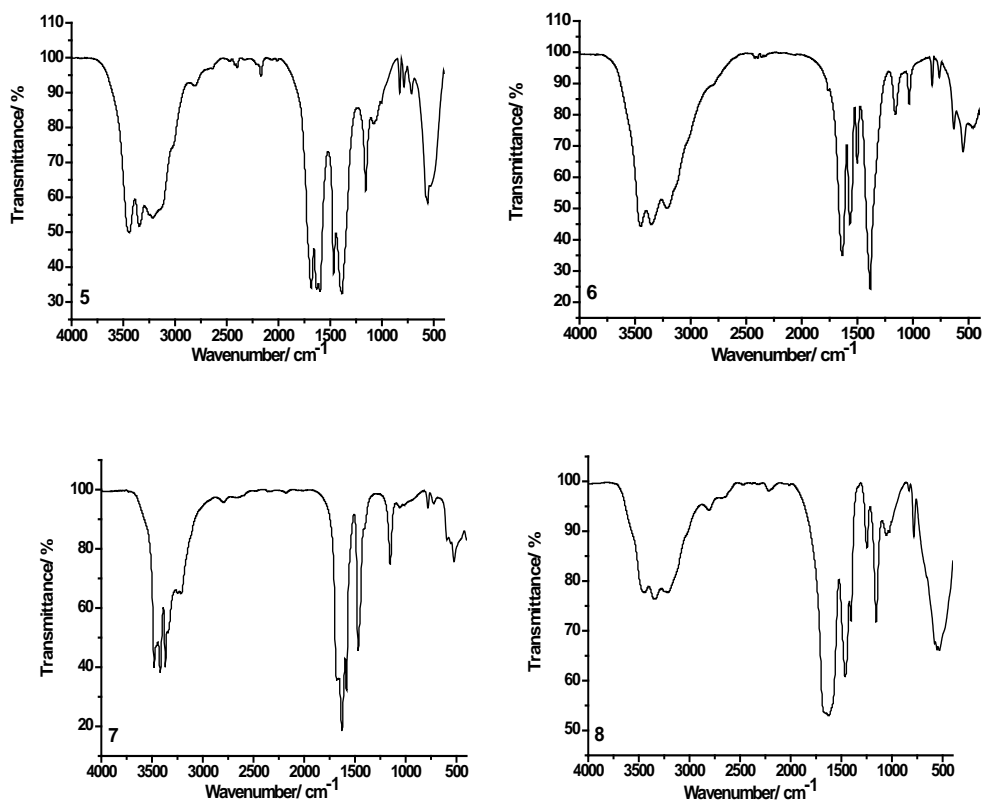


Fig. 2 Infrared spectra of urea complexes at 60 °C: $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (5), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (6), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (7) and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (8) complexes

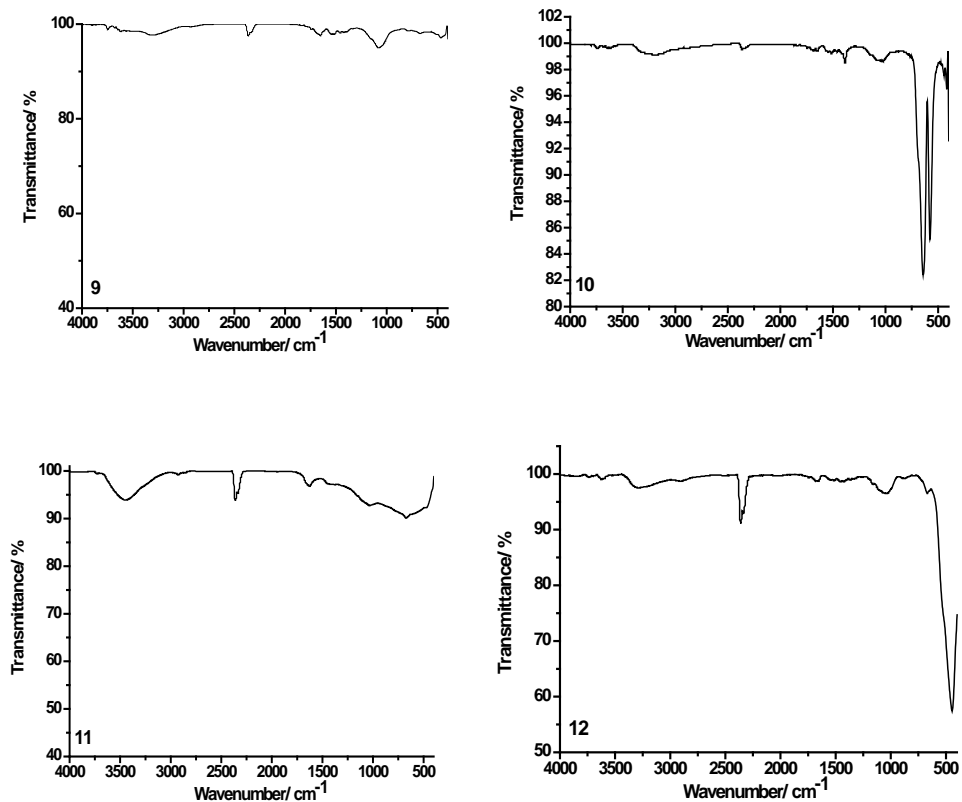


Fig. 3 Infrared spectra of urea complexes at 800 °C: AgO/Ag metal (9), Cr_2O_3 (10), CdO/Cd metal (11) and ZnO/Zn metal (12) compounds

TABLE II CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF UREA (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1) AND $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2) COMPLEXES

U	A	B	1	2	Assignments ^(b)
3450	3390 3290	3440 3330	3444 3344	3443 3345	$\nu_{\text{as}}(\text{NH}_2)$ $\nu(\text{OH}); \text{CH}_3\text{OH}$
3350	3130 3030	3190	3258	3215	$\nu_s(\text{NH}_2)$ $\nu(\text{CH}_3); \text{CH}_3\text{OH}$
1683	1725	1505	1684	1683	$\delta(\text{C}=\text{O})$
1471	1395	1505	1384	1387	$\nu(\text{C}-\text{N})$

TABLE III CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF UREA (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4) AND $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5) COMPLEXES

U	A	B	4	5	Assignments ^(b)
3450	3390 3290	3440 3330	3452 3354	3450 3353	$\nu(\text{OH}); \text{H}_2\text{O}$ $\nu_{\text{as}}(\text{NH}_2)$
3350	3130 3030	3190	3194	3211	$\nu_s(\text{NH}_2)$
1683	1725	1505	1630 1571	1635 1567	$\delta(\text{H}_2\text{O})$ $\delta(\text{C}=\text{O})$
1471	1395	1505	1497	1501	$\nu(\text{C}-\text{N})$

TABLE IV CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF UREA (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $\text{CDCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7) AND $\text{CDCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) COMPLEXES

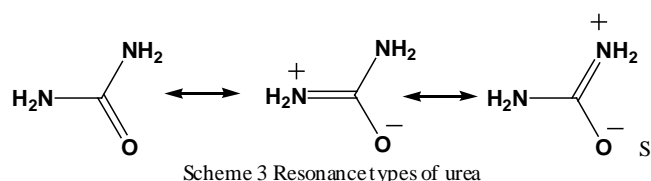
U	A	B	7	8	Assignments ^(b)
3450	3390 3290	3440 3330	3479 3420	3479 3419	$\nu(\text{OH}); \text{H}_2\text{O}$ $\nu_{\text{as}}(\text{NH}_2)$
3350	3130 3030	3190	3367 3210	3368 3211	$\nu_s(\text{NH}_2)$
1683	1725	1505	1681	1679	$\delta(\text{C}=\text{O})$
1471	1395	1505	1583	1583	$\nu(\text{C}-\text{N})$

TABLE V CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF UREA (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) AND $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) COMPLEXES

U	A	B	10	11	Assignments ^(b)
3450	3390 3290	3440 3330	3463 3351	3446 3344	$\nu(\text{OH}); \text{H}_2\text{O}$ $\nu_{\text{as}}(\text{NH}_2)$
3350	3130 3030	3190	3258	3212	$\nu_s(\text{NH}_2)$
1683	1725	1505	1630	1624	$\delta(\text{C}=\text{O})$ $\delta(\text{H}_2\text{O})$
1471	1395	1505	1462	1461	$\nu(\text{C}-\text{N})$

The assignments of full vibrational analysis of crystalline urea have been published^[38]. Tables 2 to 5 give diagnostic infrared peaks of the free urea ligand, published work and Ag(I), Cr(III), Cd(II) and Zn(II) complexes. Assignments have been given in comparison with the data obtained for the free urea, that is, uncoordinated, U^[38] and its $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ and $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ complexes^[38]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pd(II) ions in

$[\text{Pt}(\text{urea})_2\text{Cl}_2]$ coordinate to the nitrogen, whereas Fe(III), Zn(II), and Cu(II) coordinate to the oxygen of urea^[38]. The distinguished bands of $\nu(\text{C}-\text{N})$ are exhibited at lower wave numbers in the spectra of $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1) and $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2) complexes than for free urea, whereas the $\nu(\text{C}=\text{O})$ band shows a frequency at the same wave number of free urea. These shifts are consistent with nitrogen coordination, suggesting the presence of $+\text{N}=\text{C}-\text{O}-$ resonance features^[51], see Scheme 3.



Concerning $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (**4**), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (**5**), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (**7**), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (**8**), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (**10**) and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (**11**) complexes, the coordination mode takes place *via* oxygen of amide group, the positively charged metal ion stabilizes the negative charge on the oxygen atom; the NCO group now occurs in its polar resonance form and the double bond character of the CN bond increases or is still not affected, while the double bond character of the CO bond decreases, resulting in an increase of the CN stretching frequency with a simultaneous decrease in the CO stretching frequency^[52,53].

The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $(3400 \sim 3450) \text{ cm}^{-1}$, while the corresponding bending motion of the uncoordinated water, $\delta(\text{H}_2\text{O})$, is observed in the range of $(1630 \sim 1638) \text{ cm}^{-1}$.

In both silver complexes, the characteristic stretching vibrations of the nitrate group, NO_3^- , is observed at around $(1385 \text{ cm}^{-1}$ and 1160 cm^{-1} attributed to $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$, respectively^[54]. The stretching motion of $(\nu(\text{N=O}))$ is observed at 1475 cm^{-1} as a strong band, while the bending motion of the type $\delta(\text{NO}_2)$ are well resolved and observed at 786 as a medium band.

D. $^1\text{H-NMR}$ Spectral Analysis

$^1\text{H-NMR}$ data were assignment in parts per million (ppm), and they were referenced internally to the residual proton impurity in DMSO (dimethylsulfoxide). The $^1\text{H-NMR}$ spectra of the $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (**7**), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (**8**), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (**10**) and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (**11**) complexes (Fig. 4) are consistent with the suggested formulas, scheme 4. The $^1\text{H-NMR}$ spectral data of Cd(II) and Zn(II) complexes were reported in Table 6.

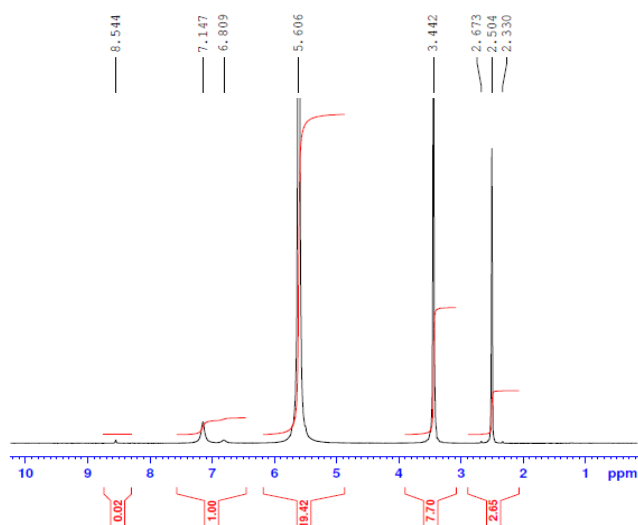


Fig. 4A $^1\text{H-NMR}$ spectrum of $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (**7**) complex

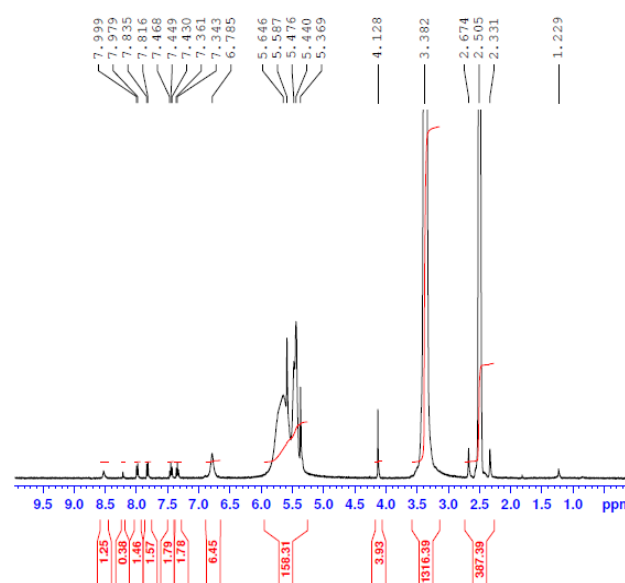


Fig. 4B $^1\text{H-NMR}$ spectrum of $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (**8**) complex

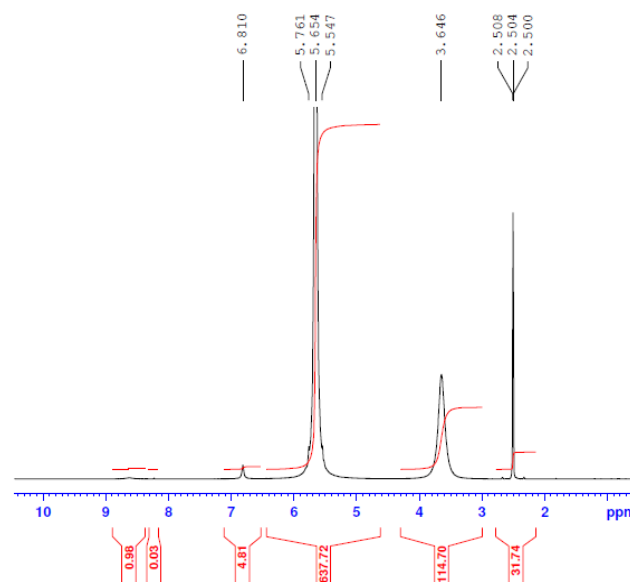


Fig. 4C $^1\text{H-NMR}$ spectrum of $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (**10**) complex

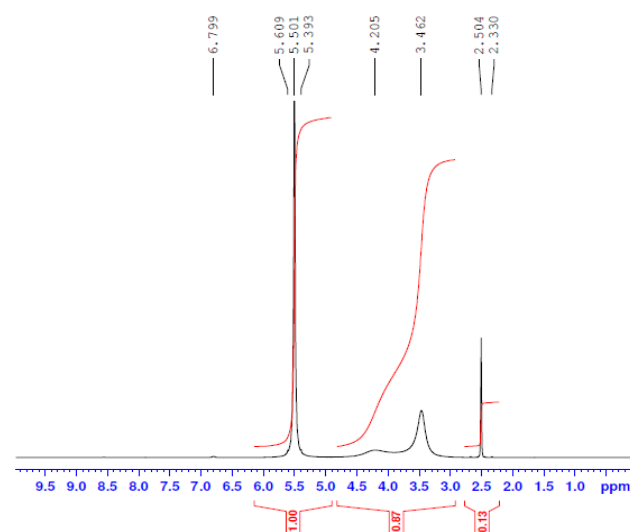
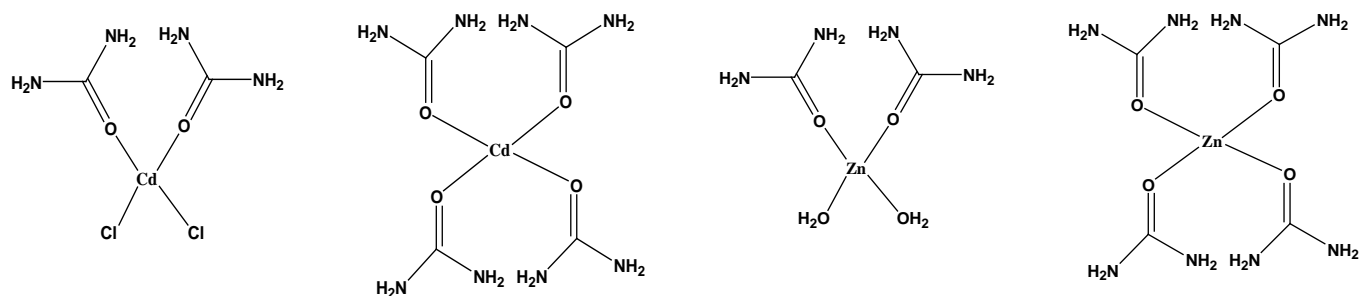


Fig. 4D $^1\text{H-NMR}$ spectrum of $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (**11**) complex



Scheme 4 Suggested structure of Cd(II) and Zn(II) urea complexes (7, 8, 9 and 10)

TABLE VI ^1H -NMR SPECTRAL BANDS (PPM) AND TENTATIVE ASSIGNMENTS OF $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) AND $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) COMPLEXES

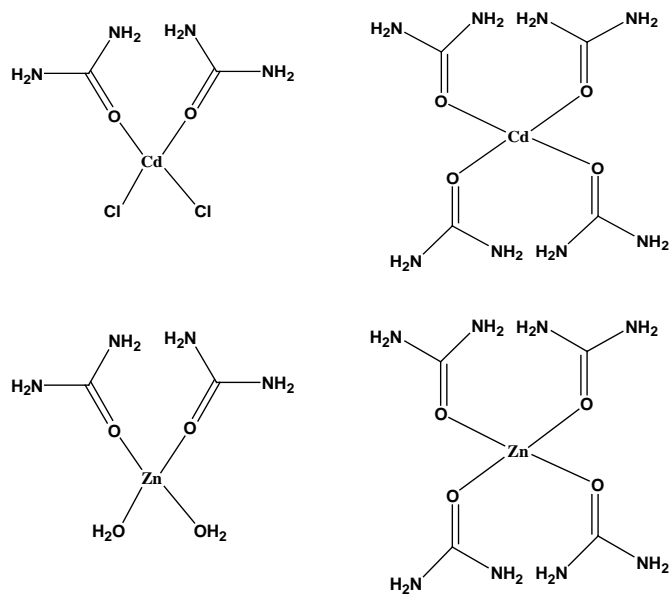
urea	ppm				Assignments (b)
	7	8	10	11	
5.600	3.442	4.128	3.646	3.462	\square ; $-\text{NH}_2$
---	5.606–8.544	5.369–7.999	5.547–5.761	5.393–5.609	\square ; $+\text{NH}_2$

In the free urea ligand, the only one peak at 5.6 ppm is assigned to (4H; 2NH₂) four protons of two symmetric amino groups. Upon the complexation of Cd(II) and Zn(II) via oxygen atom and the resonance case in scheme 3, the discussion of the upfield and downfield status for the protons concerning $-\text{NH}_2$ group is due to the formation of new metal complexes chelating. Compared with the ^1H -NMR spectrum data of pure urea, the ^1H -NMR spectra of the Cd(II) and Zn(II) complexes exhibits two types of $-\text{NH}_2$ groups one of them neutral and the other one has a positively charged $=^+\text{NH}_2$, so the value of protons for $-\text{NH}_2$ group is appeared with upfield chemical shift at 3.442, 4.128, 3.646 and 3.462 ppm, for $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) and $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ complexes, respectively. On the other hand, the protons of $=^+\text{NH}_2$ group is downfield and presented at (5.606~8.544 ppm), (5.369~7.999 ppm), (5.547~6.810 ppm) and (5.393~6.799 ppm), respectively, for complexes 7, 8, 10 and 11. According to this result, it can be deduced that the electronic environments of the urea protons change with the formation of the new complexes.

E. Thermal Analysis

The $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8), $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10), and

$\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) complexes were studied by thermogravimetric analysis from ambient temperature to 800°C in oxygen atmosphere. Figures 5A-D and 6A-D and Tables 7 and 8 illustrate TG curves and decomposition stages obtained for these complexes with a temperature rate 30°C/min.



Scheme 4: Suggested structure of Cd(II) and Zn(II) urea complexes (7, 8, 9 and 10)

TABLE VII THE MAXIMUM TEMPERATURE, $T_{\text{MAX}}/^\circ\text{C}$, AND WEIGHT LOSS VALUES OF THE DECOMPOSITION STAGES FOR THE $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), AND $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10) COMPLEXES

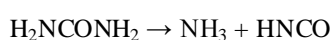
Complexes	Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost		
			species	% Weight loss	
1	First step	237	6CH ₃ OH	39.14	39.84
	Second step	299	NO ₃	12.49	12.86
	Third step	381	Urea	11.08	12.44
	Fourth step	492	CH ₄ + N ₂	10.55	9.13
	Residue		AgO	26.73	25.73
4	First step	123	2H ₂ O	7.69	7.28

	Second step	207	2.5H ₂ O	8.34	9.10
	Third step	273	6H ₂ O+3HCl	41.94	43.98
	Fourth step	509	2Urea	24.63	24.26
	Residue		CrO _{1.5}	17.39	15.37
7	First step	252	Cl ₂ +H ₂ O	28.04	27.70
	Second step	317, 404, 656	2Urea	37.39	37.34
	Residue		Cd metal	34.57	34.98
10	First step	244	4H ₂ O+Cl ₂ +Urea	44.48	45.28
	Second step	354, 561	3Urea	40.74	40.15
	Residue		Zn metal	14.77	14.59

TABLE VIII THE MAXIMUM TEMPERATURE, $T_{\text{MAX}}/^{\circ}\text{C}$, AND WEIGHT LOSS VALUES OF THE DECOMPOSITION STAGES FOR THE $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5), $\text{CDCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) AND $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) COMPLEXES

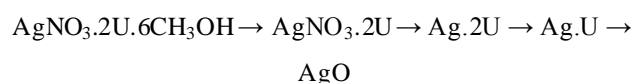
Complexes	Decomposition	$T_{\text{max}}/^{\circ}\text{C}$	Lost species	% Weight loss	
				Found	Calc.
2	First step	149	CH ₃ OH	8.17	9.94
	Second step	243, 297, 384	Urea + NO ₃	37.38	37.90
	Third step	495	Urea	20.42	18.64
	Residue		Ag	34.24	33.55
5	First step	234	7.5H ₂ O+3HCl+4Urea	83.55	82.15
	Residue		CrO _{1.5}	16.45	17.85
8	First step	213	Urea + H ₂ O	17.22	17.66
	Second step	275	Urea + ½Cl ₂	19.50	21.63
	Third step	373	Urea	13.42	13.60
	Fourth step	690	Urea + ½Cl ₂	47.15	47.11
	Residue		Contaminated carbon	2.71	---
11	First step	95	2.5H ₂ O	11.79	12.35
	Second step	239	1.5H ₂ O+Cl ₂ +2H ₂ O	37.34	36.78
	Third step	349	Urea	15.05	16.47
	Fourth step	563	Urea + loss Zn metal	28.29	26.87
	Residue			7.53	7.53

Thermal analysis of $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1) complex (Fig. 5A) shows that the silver(I) complex prepared at room temperature is thermally stable up to 145°C. Its thermal decomposition occurs in four stages of weight loss of different intermediates followed by four endothermic maximum temperatures $\text{DTG}_{\text{max}} = 237, 299, 381$ and 492°C, respectively. From the TG-DTG curves it is clear that the first decomposition stage from 145 to 279°C corresponds to the loss of six methanol molecules (39.14% experimental loss; 39.84% theoretical loss). The continued loss, decomposition steps second and third up to 416°C corresponds to the complete decomposition of the nitrate, NO₃⁻, and one urea molecules (12.49% experimental loss; 12.86% theoretical loss) and (11.08% experimental loss; 12.44% theoretical loss) followed by endothermic DTG_{max} at 299°C and 381°C, respectively. The most probable thermal decomposition of urea from the complex may be represented as:



As the temperature is raised to 596°C, the complete loss of second urea molecule (10.55% experimental loss; 9.13% theoretical loss) and conversion to silver(I) oxide. Based on the results of thermal analysis of residual

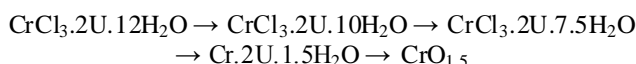
supported by the infrared spectra (Fig. 3), XRD, EDX and SEM measurements, the mechanism of the thermal decomposition of the complex is proposed as:



The TG curve of the $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ complex has a three stages of the dissociation of complex are indicated in TG and DTG curve. The decomposition starts from 43°C and ends at 201°C, the mass loss experimentally is 8.17% against theoretically 9.94%, corresponding to the release of 1 mol of methanol. The second stage is a wide scale that started from 201 to 420°C with three $\text{DTG}_{\text{max}} = 243, 297$ and 384°C, respectively. The mass loss experimentally is 37.38% against theoretical 37.90%, showing that 1 mol urea and NO₃⁻ ion is liberated. The third stage is in continuation with the second stage from 420 to 489°C with maximum peak at 495°C. The experimental mass loss is 20.42% against theoretical mass loss of 18.64%, corresponding to the dissociation of 1 mol of urea. The residual product is silver metal, comparable with the final decomposition product of $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ which gave silver(I) oxide at the final decomposition stage, that we can discuss this

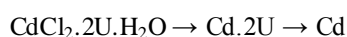
differentiate according to the solvent effect. The product of thermal decomposition was analyzed by the infrared and X-ray powder diffraction measurement.

The TG-DTG curve of $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4) complex indicates the dissociation of complex in four stages. The first transition changes from 42 to 166°C, and the experimental mass loss is 7.69% against the theoretical mass loss of 7.28%, corresponding to the release of 2 mol of water. The second transformation is from 166 to 237°C, and the mass loss experimental is 8.34% against the theoretical loss of 9.10%, due to the release of 2.5 mol of water. The third stage is in continuation with the second stage from 237 to 480°C. The mass loss experimentally is 41.94% against theoretical mass loss of 43.98%, corresponding to the dissociation of 6 mol of water and 3 mol HCl. The fourth stage is from 480 to 563°C. The experimental mass loss is 17.39%, showing that 2urea are dissociated. The experiment result is matched with theoretical value. The final product is considered to be $\text{CrO}_{1.5}$. The thermo analytical data for $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4) complex are also given in Table 7. All transitions in DTG curve corresponding to the transition are observed in the TG curve and recorded at $\text{DTG}_{\text{max}} = 123, 207, 273$ and 509°C , respectively. The final decomposition step led to formed chromium oxide Cr_2O_3 . The sequential thermal dissociation process of the complex is shown as follows:



The thermoanalytical data for $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ complex are listed in Table 8. There is one very strong endothermic peak in DTG curve corresponding to the chemical events observed in the TG curve. Weight loss in the range of 39 to 270°C with $\text{DTG}_{\text{max}} = 234^\circ\text{C}$ is experimental to be 83.55% which is close to theoretical value 82.15%, indicating loss of 7.5 mol of water, 4 mol of urea and 3 mol of HCl. At 270°C weight of residual Cr_2O_3 oxide polluted with carbon atoms was experimental to be 16.45% which is close to theoretical value 17.84%. The final thermal decomposition was checked using IR, XRD, SEM and EDX measurements.

The TG-DTG curve of $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ complex has two stages the transitions observed in the TG-DTG curve. The first transition changes from 167 to 293°C with $\text{DTG}_{\text{max}} = 252^\circ\text{C}$, and the experimental mass loss is 28.04% against the theoretical loss of 27.70%, corresponding to the release of 1 mol of water and 1 mol of Cl_2 . The second transition stage is a large scale which started from 293 to 713°C , with three DTG_{max} at 317, 404 and 656°C . The experimental mass loss is 37.39% against the theoretical mass loss of 37.34%, due to the release of 2 mol of urea. The final product is considered to be Cd metal. The disturbed in the arrangement of the decomposition stages back to the lower melting and boiling points of cadmium metal which occurs at 321°C and 767°C , respectively. The sequential thermal dissociation process of the complex is shown as follows:



$\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ complex: in the range of 135 – 766°C , four DTG_{max} at 213°C , 275°C , 373°C and 690°C with four mass loss stages are exhibited. The Table 8 summarized the thermoanalytical and weight loss obtained data. The thermal transformation starts with an endothermic peak existing on DTG curve with $\text{max} = 213^\circ\text{C}$. This stage of decomposition corresponds to experimental mass loss of 17.22%, which can be attributed to the loss of one urea ligand and the decomposition of 1 mol water. The second stage with experimental mass loss of 19.50% and theoretical mass loss of 21.64% may result from decomposition of the 1 mol urea and half mol of chlorine gas. The third and fourth decomposition stages amount to a total experimental mass loss of 60.57% with theoretical mass loss of 60.71%, which assigned to the loss of 2urea and half chlorine molecules. The decline in output of the final product was discussed according the previous notification concerning the lower melting and boiling points of cadmium metal.

The zinc(II) urea complex which was prepared at room temperature, $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$, shows two main stages of decomposition as is evident from DTG peaks at 244°C and (354°C and 561°C), and is thermally stable up to 127°C . The first stage of decomposition with experimental mass loss of 44.48% and theoretical mass loss of 45.28% may be assigned to the decomposition of 4 mol water, 1 mol Cl_2 and 1 mol urea. The second stage, amounting to experimental mass loss of 40.74% in good agreement with theoretical mass loss of 40.15%, may be attributed to the loss of the remaining three urea ligand molecules, resulting in the final residue of zinc metal.

The TG curve for $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ complex has three stages of mass losses within the temperature range of 29 – 653°C at 95°C , 239°C , 349°C and 563°C DTG maximum peaks. The first stage at 29 – 151°C with experimental mass loss of 11.79% (theoretical: 12.35%) corresponds to the loss of 2.5 H_2O molecules. The second stage at 151 – 311°C with experimental mass loss of 37.34% (theoretical: 36.78%) corresponds to the loss of 3.5 H_2O and Cl_2 molecules. The third stage of decomposition at the temperature range of 311 – 467°C is assigned to the loss of one molecule of urea ligand with experimental mass loss of 15.05% (theoretical: 16.47%). The fourth decomposition stage is distorted, which may be assigned to decomposition of the second urea molecule and loss a part of zinc metal, so the experimental mass loss shifted to higher percentage of 28.29% than expected value of 16.47%. This can be explained through the formation of zinc(II) chloride as an intermediate which has a low melting and boiling degrees at 292°C and 756°C .

To clarify the final decomposition products of urea complexes, the solid residues after thermal degradation under oxygen atmosphere were collected at 800°C and were analyzed by infrared spectroscopy, X-ray diffractometry, EDX and SEM.

F. X-ray Powder Diffraction Studies

The x-ray powder diffraction patterns for the Ag(I), Cr(III), Cd(II) and Zn(II) urea at different temperatures with

formulas; $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (1), $\text{AgNO}_3 \cdot 2\text{U} \cdot \text{CH}_3\text{OH}$ (2) and Ag metal (3), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (4), $\text{CrCl}_3 \cdot 4\text{U} \cdot 9\text{H}_2\text{O}$ (5) and Cr_2O_3 (6), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (7), $\text{CdCl}_2 \cdot 4\text{U} \cdot \text{H}_2\text{O}$ (8) and CdO (9) and $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (10), $\text{ZnCl}_2 \cdot 2\text{U} \cdot 6\text{H}_2\text{O}$ (11) and ZnO (12) are depicted in Fig. 7A-D. Inspecting these patterns, we notice that all systems are well crystalline except for diagrams of silver(I) complex at 800 °C and $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ complex. The crystallite size of these complexes could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Debye-Scherrer Equation 1^[55]. Where D is the particle size of the crystal grain, K is a constant (0.94 for Cu grid), λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size located within nano scale range.

$$D = K\lambda / \beta \cos\theta \quad (1)$$

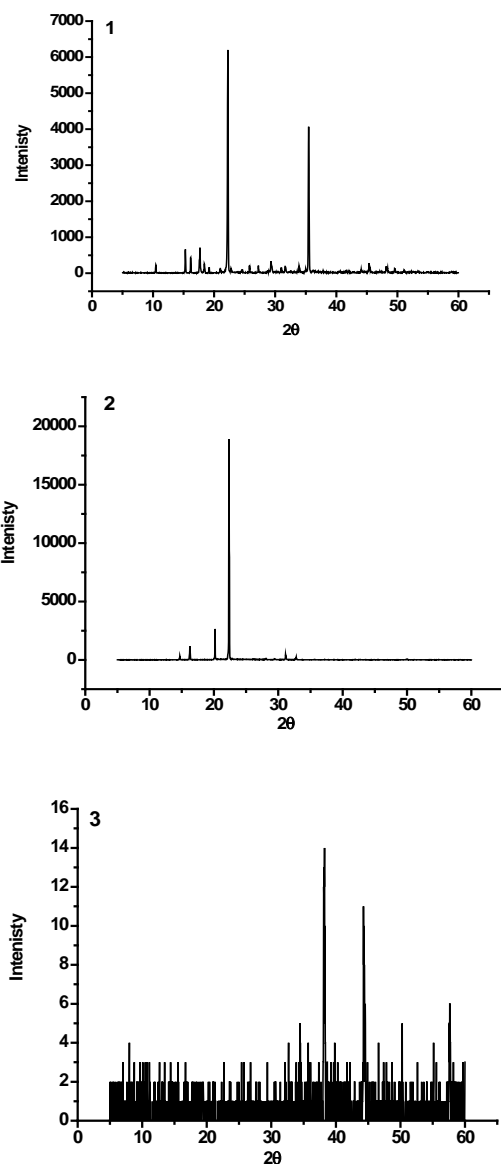


Fig. 7A XRD spectra of the compounds resulted from the reaction of silver(I) nitrate with urea at room (1), 60 °C (2) and 800 °C (3) temperatures

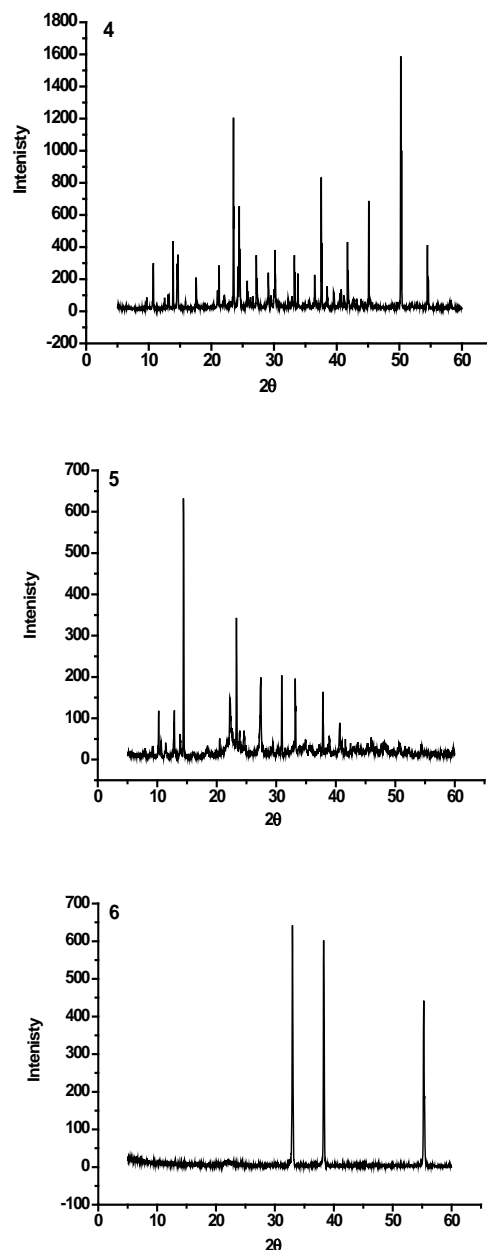
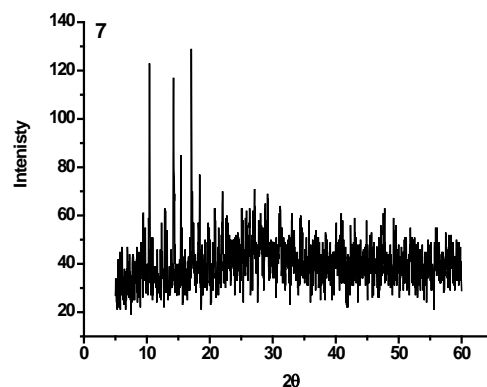


Fig. 7B XRD spectra of the compounds resulted from the reaction of chromium(III) chloride with urea at room (4), 60 °C (5) and 800 °C (6) temperatures



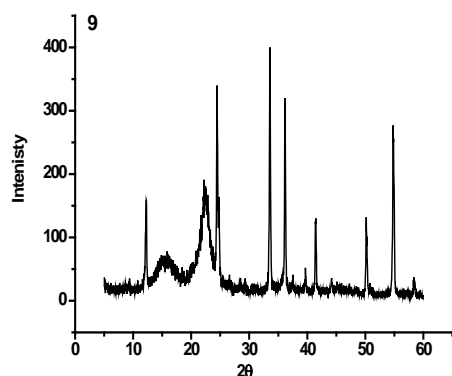
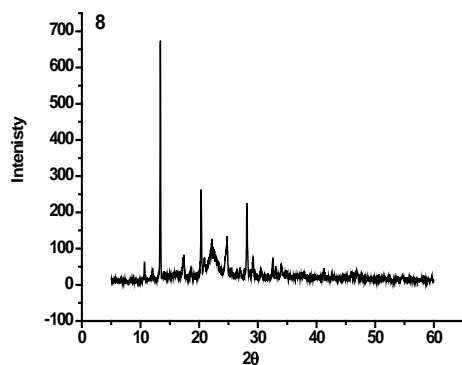


Fig. 7C XRD spectra of the compounds resulted from the reaction of cadmium(II) chloride with urea at room (7), 60 °C (8) and 800 °C (9) temperatures

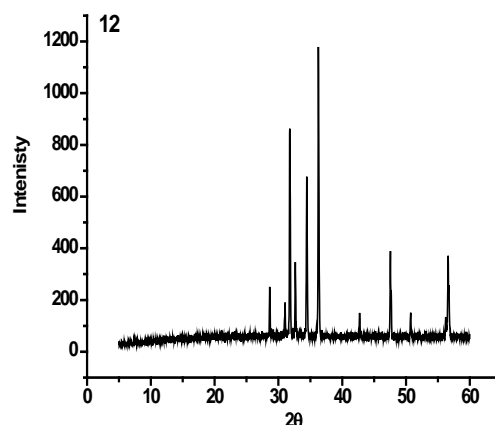
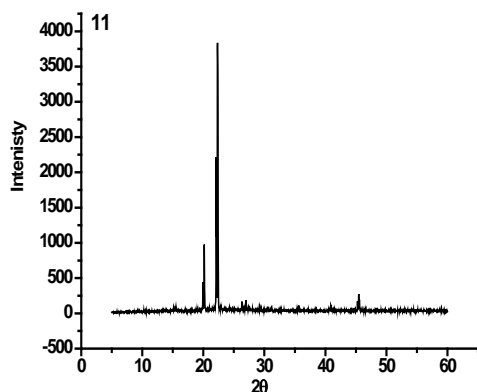
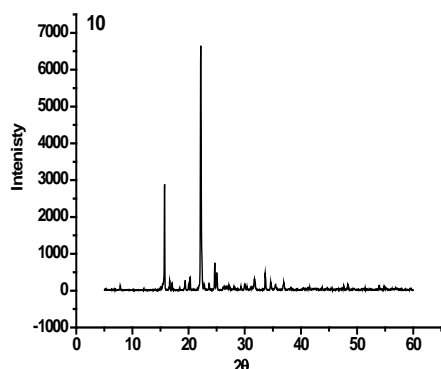


Fig. 7D XRD spectra of the compounds resulted from the reaction of zinc(II) chloride with urea at room (10), 60 °C (11) and 800 °C (12) temperatures

G. SEM and EDX Studies

Scanning electron microscopy is a simple tool used to give an impression about the microscopic aspects of the physical behavior of urea as a chelating agent (Figs. 8A-D). Although this tool is not a qualified method to confirm complex formation but it can be a reference to the presence of a single component in the synthetic complexes. The pictures of the Ag(I), Cr(III), Cd(II) and Zn(II) complexes show a small particle size with an nano feature products. The chemical analysis results by EDX for the formed complexes show a homogenous distribution in between metal ions and chelating agent. SEM examinations were checked the morphology of the surfaces of these complexes that show small particles which tend to agglomerates formation with different shapes comparison with the start materials. The peaks of EDX profile of these complexes (Figs. 9A-D) refer to all elements which constitute the molecules of urea complexes (1-to-12) that clearly identified confirming the proposed structures

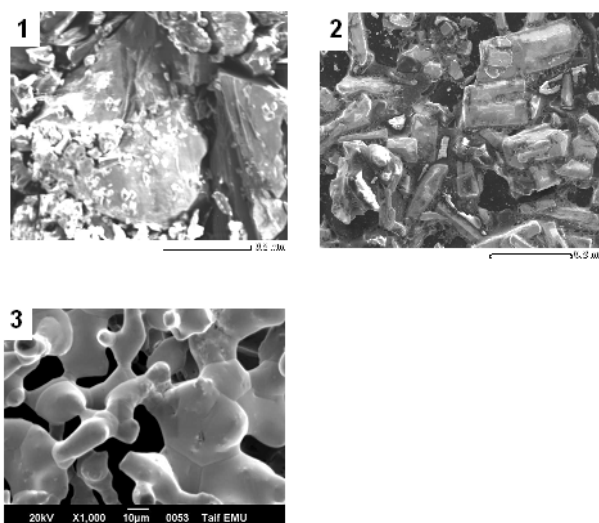


Fig. 8A SEM image of the compounds resulted from the reaction of silver(I) nitrate with urea at room (1), 60 °C (2) and 800 °C (3) temperatures

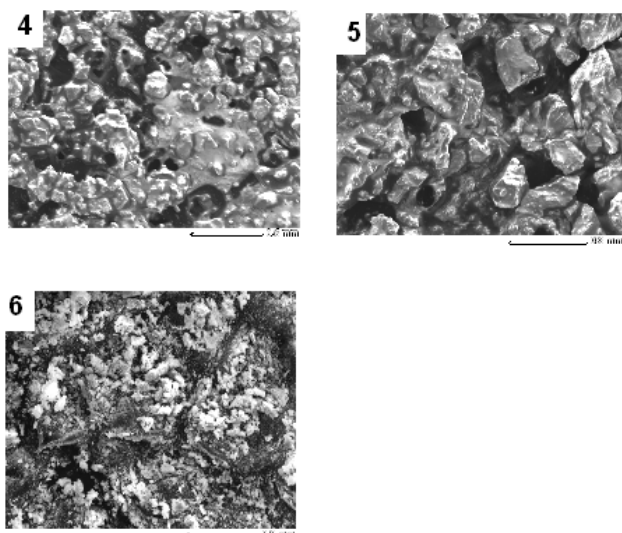


Fig. 8B SEM image of the compounds resulted from the reaction of chromium(III) chloride with urea at room (4), 60 °C (5) and 800 °C (6) temperatures

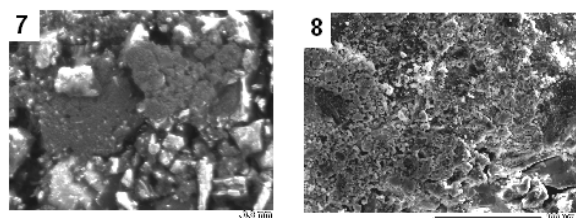


Fig. 8C SEM image of the compounds resulted from the reaction of cadmium(II) chloride with urea at room (7), 60 °C (8) and 800 °C (9) temperatures

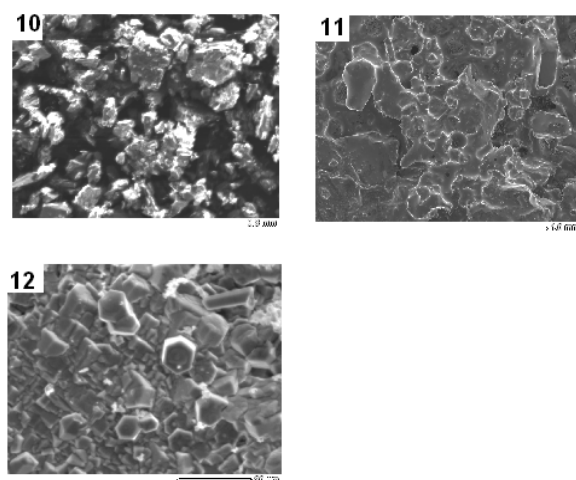


Fig. 8D SEM image of the compounds resulted from the reaction of zinc(II) chloride with urea at room (10), 60 °C (11) and 800 °C (12) temperatures

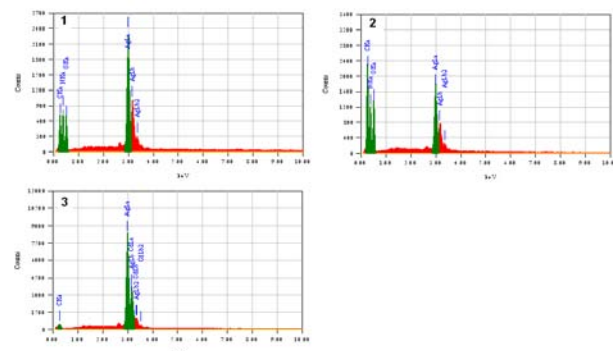


Fig. 9A EDX diagram of the compounds resulted from the reaction of silver(I) nitrate with urea at room (1), 60 °C (2) and 800 °C (3) temperatures

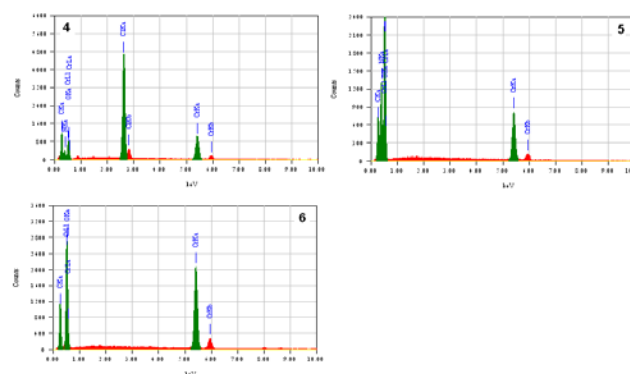


Fig. 9B EDX diagram of the compounds resulted from the reaction of chromium(III) chloride with urea at room (4), 60 °C (5) and 800 °C (6) temperatures

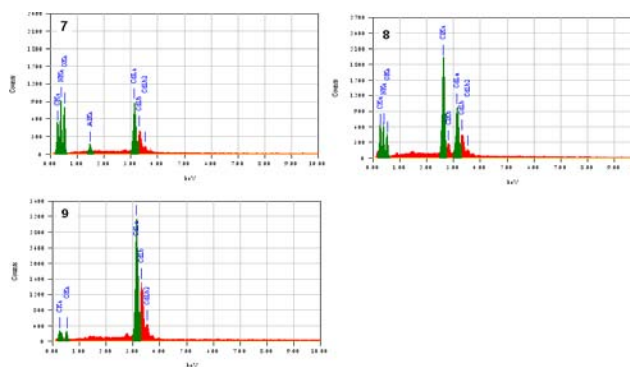


Fig. 9C EDX diagram of the compounds resulted from the reaction of cadmium(II) chloride with urea at room (7), 60 °C (8) and 800 °C (9) temperatures

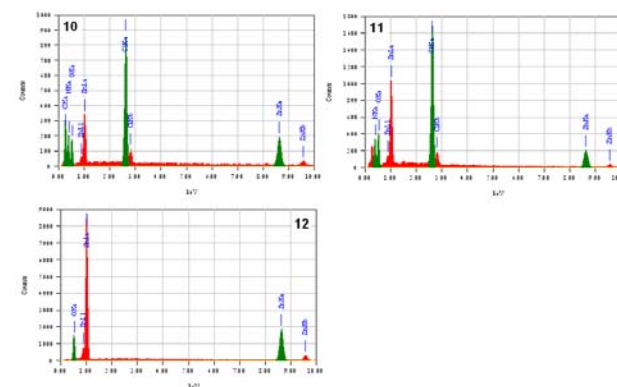


Fig. 9D EDX image of the compounds resulted from the reaction of zinc(II) chloride with urea at room (10), 60 °C (11) and 800 °C (12) temperatures

H. Biological Evaluation

Biological evaluations were checked in term of antimicrobial activities of target compounds against gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and tow strains of fungus (*Aspergillus flavus* and *Candida albicans*). Result from the agar disc diffusion tests for antimicrobial activities of target compounds are presented in Table 9, and illustrated in Fig. 10. The diameters of zone of inhibition (in mm) of the standard drug tetracycline against gram positive bacteria *B. subtilis* and *S. aureus* and gram negative bacteria *E. coli* and *P. aeruginosa*

were found to be 36, 30, 31 and 35 mm, respectively, while the standard drug amphotericin B against *Aspergillus flavus* and *Candida albicans* gave 18 and 19, respectively. Under identical conditions, Table 9 shows that, Complex **1** has (14, 12, 12, 15, 0.0 and 0.0 mm), Complex **4** has (12, 16, 11, 12, 0.0 and 0.0 mm), Complex **7** has (24, 21, 23, 21, 18 and 12 mm), and Complex **10** has (19, 23, 26, 24, 0.0 and 0.0 mm), respectively, for *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Aspergillus flavus* and *Candida albicans*. All complexes were found to be efficiency antimicrobial agents except for **1**, **4**, and **10** complexes have no efficiency against *Aspergillus flavus* and *Candida albicans* fungus.

TABLE IX INHIBITION ZONE DIAMETER (MM) OF THE TARGET COMPOUNDS AGAINST TESTED MICROORGANISMS FOR $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (**1**), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (**4**), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (**7**), AND $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (**10**) COMPLEXES

Sample		Inhibition Zone Diameter (Mm /Mg Sample)					
		<i>Bacillus Subtilis</i> (G ⁺)	<i>Escherichia Coli</i> (G ⁻)	<i>Pseudomonas Aeruginosa</i> (G ⁻)	<i>Staphylococcus Aureus</i> (G ⁺)	<i>Aspergillus Flavus</i> (Fungus)	<i>Candida Albicans</i> (Fungus)
Standard	Control: DMSO	0.0	0.0	0.0	0.0	0.0	0.0
	Antibacterial agent (Tetracycline)	36	31	35	30	--	--
	Antifungal agent (Amphotericin B)	--	--	--	--	18	19
	1	14	12	12	15	0.0	0.0
	4	12	16	11	12	0.0	0.0
	7	24	21	23	21	18	12
	10	19	23	26	24	0.0	0.0

G: Gram reaction.

Solvent: DMSO.

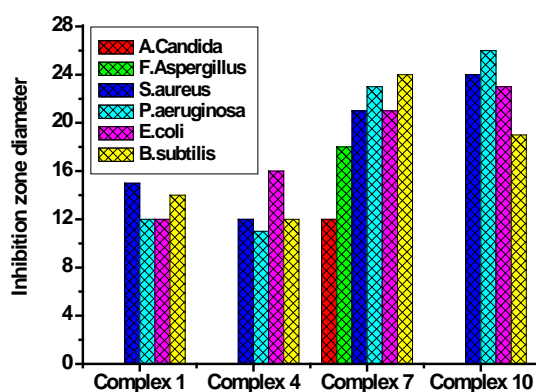


Fig. 10 Biological evaluation diagram of $\text{AgNO}_3 \cdot 2\text{U} \cdot 6\text{CH}_3\text{OH}$ (**1**), $\text{CrCl}_3 \cdot 2\text{U} \cdot 12\text{H}_2\text{O}$ (**4**), $\text{CdCl}_2 \cdot 2\text{U} \cdot \text{H}_2\text{O}$ (**7**), and $\text{ZnCl}_2 \cdot 4\text{U} \cdot 4\text{H}_2\text{O}$ (**10**) complexes

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